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Copper Sensor System for Unattended Marine Operations III: Detecting Copper(I) in the Marine Environment with Fiber Optic Technology

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Since the ionic forms of copper(I) and copper(II) are toxic in the marine environments, a portable and easy-to-use rapid-measurement sensor capable of measuring parts per billion (ppb) levels of ionic copper [copper(I) and copper(II)] in the marine environment is needed. This study tests the hypothesis that the organic reagent bathocuproine (BCP) can be immobilized to develop a fiber optic sensor capable of measuring copper(I) in seawater. This work describes the response of a first-generation fiber optic/copper(I) probe. Results indicate that the fiber optic probe has sensitivity in the ppb range with a lower detection limit of 17 ppb. In addition, reduction of copper(II) to copper(I) using hydroxylamine hydrochloride allows the fiber optic probe to determine total ionic copper.

14. SUBJECT TERMS

Optical sensor	Nafion	Trace metals
Bathocuproine	Anti-fouling paint	
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TABLE OF CONTENTS

COPPER SENSOR SYSTEM FOR UNATTENDED MARINE OPERATIONS III: DETECTING COPPER(I) IN THE MARINE ENVIRONMENT WITH FIBER OPTIC TECHNOLOGY

Executive Summary

A major source of trace metal contamination in the marine environment comes from the copper containing anti-fouling paints on ship hulls. In the environment, an anti-fouling paint containing copper (I) presents a challenge because its design is to leach continuously over a period of time. It is a pesticide that kills or prevents attachment of organisms to a ship hull, but, also is a source of introduced copper (I).

This study tests the hypothesis that the organic molecule, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine=BCP) imbeded in a C_{18} polymer bead is capable of measuring copper (I) in seawater. The purpose is to develop a sensor system that will measure copper (I) contamination quickly. The sensor must have

- parts per billion (ppb) detection limits,
- marine environmental immersion capability, and
- the ability to detect the copper (I) oxidation state.

An easily and readily deployed sensor can yield results that will allow the deployment of remedial methods to avert an environmental problem.

The sensor uses a C_{18} polymer bead impregnated with Bathocuproine (BCP) and attached to a bifurcated fiber-optic cable. BCP will react with copper(I) turning a shade of orange. The orange shade is relatve to the Cu(I) concentration. As such the intensity of the color change is measurable using a spectrometer coupled to the fiber-optic cable.

The conclusions from this phase of the study are:

- that the chemical procedure using the BCP C_{18} polymer bead is a way to test for total available ionic copper [(I) and (II)];
- that the chemical procedures are reproducible and robust; and
- that the C_{18} polymer bead presents a method for further study.

INTRODUCTION

Harbors and marinas are point sources for trace metal contamination in the aquatic environment (Hall et al 1990; Moffett et al 1997; Foerster et al 1999). Within these basins, moored ships, and ships undergoing hull cleaning, contribute trace metals (Nriagu 1979). Specifically, the major contributor to the input of trace metals is the anti-fouling paint used on the hulls to prevent biological fouling (Claisse and Alzieu 1993; Hare 1994). Because of the widespread use of copper-based anti-fouling paints, copper has become a major source of trace metal contamination in the marine environment (Nriagu 1979).

The copper(I) and copper(II) ionic forms are the most toxic in the marine environment when they exist as the free ion, i.e., not complexed with naturally occurring ligands (Tessier and Turner 1995). Above low ppb levels, the free ion form of copper is poisonous to marine plant photosynthesis and marine animal life (Vymazal 1995; Sorensen 1991). Naturally occurring ligands act as scavengers for the free copper ion by binding it and rendering it non-bioavailable (Coale and Bruland 1990).

Therefore, the free ion concentrations, or a measure of the dissolved copper(I) and copper(II) in water, are indicative of levels of toxicity in the water column. Complexed copper is not immediately toxic. Most standard analytical techniques require some sort of pretreatment prior to analysis in order to differentiate free ion from complexed ion. This pretreatment procedure increases the overall analysis time as well as potentially introducing contamination. Hence, the development of an in-situ, real time technique for the detection of copper(I) and copper(II) is warranted.

Colorimetric and fluorimetric techniques use metal specific dyes which change their absorption or fluorescence emission properties when complexed with trace metal ions. These techniques are adaptable to fiber optic technology (Ervin et al 1993; Seitz et al 1985). In this study, the major goal is the identification and immobilization of a photochromic reagent sensitive enough to respond to low concentrations (ppb) of the copper ion.

A standard spectrophotometer technique for determination of total copper in natural waters uses the colorimetric reagent 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, or bathocuproine- disulfonate (BCS) (Greenberg et al 1992). It takes two molecules of BCS to complex with 1 molecule of copper(I)(Diehl and Smith 1972). The resulting copper(I)-BCS complex exhibits an absorption peak between 479-484 nm with a molar absorptivity of 12,250-14,160 L^{-1} Mol^{-1} depending on the solvent (Greenberg et al 1992; Diehl and Smith 1972).

In order to develop a sensor system applicable to aqueous environments, it is necessary to use the water insoluble desulfonated derivative of BCS,

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2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP). Once immobilized on a support medium, it will react with copper(I) ions to form the copper(I) -BCP complex which absorbs light to produce the characteristic orange color. The formation constant (Log β) for the copper(I)-BCP complex is 19, while the copper(II)-BCP complex formation constant (Log β) is 11. This imparts a high degree of selectivity for copper(I) over copper(II) as well as other trace metal ions (Coale and Bruland 1990). In order to measure total copper, more specifically the copper(II) portion, it is necessary to add the reducing agent hydroxylamine hydrochloride to the sample. This converts all the copper(II) to the copper(I) state. Once converted the total copper is quantifiable via the BCP reaction.

Because BCP exhibits such a high selectivity for copper(I), and by using additional chemistry for the measurement of copper(II), it is possible to prepare an in-situ sensor capable of detecting both species of ionic copper. The in-situ sensor is a fiber optic probe onto which the BCP is immobilized. This work describes the response of a first generation fiber optic sensor to detect copper(I) and copper(II) in seawater.

ANALYTICAL METHODS

The fiber optic sensor consisted of a bifurcated fiber optic probe containing two optical fibers (250 micron core diameter). The probe was constructed by press fitting both fibers into the end of a glass pipette (Figure 1). In this manner, both fibers were held together rigidly with both tips parallel to one another at the end of the pipette tip. The other ends of the fibers were connectorized using standard SMA connectors. One fiber was connected to the light source (Ando), and the other end connected to the fiber optic spectrometer (Ocean Optics 1000)(Figure 1).

The optical transducer was prepared by impregnating 10^{-3} Molar BCP into C_{18} resin beads which were then coated with liquid Nafion-117® and allowed to set for approximately 2 minutes. After 2 minutes, a bead (~ 2mm diameter) of the composite material was affixed to the end of the optical fiber tips in the pipette by dip coating. After attachment, the optical fiber probe was set aside and allowed to cure for one day. Following this curing process, the probe was immersed in deionized water for 24 hours in order to fully hydrate it. Prior to making copper(I) measurements in seawater, the probe was equilibrated in test medium having a salinity of 35.2 ppt for 24 hours. After equilibration, the probe was placed into seawater containing copper(I) leached from coupons coated with copper(I)-based anti-fouling paint.

Microscope slides and microscope slide cover plates were cleaned in nitric acid, washed with deionized water and painted via dip coating with

copper(I) based anti-fouling paint (Lamontagne et al 1998). The anti-fouling paint, Interviron Anti-Fouling Red Paint (Product #BRA640, Batch #UUA11176E) was obtained from Courtaurus Coatings, Inc., Houston, TX. After curing and before use, the painted coupons were preconditioned for 5 days in seawater.

In the first test of the probe response, three preconditioned coupons (total area=118.5cm^2) were placed into 2 L of stirred seawater at 24°C. The probe, consisting of the Nafion/C_{18}/BCP composite transducer, was transferred from the clean seawater sample and placed into the seawater/leached copper sample. The absorbance was monitored at a λ_{max} absorbance for the copper(I)-BCP complex (467 nm) and data was collected until a maximum absorbance was achieved (73 min.). After 73 minutes, the absorbance peak was significantly above the background to be called a real peak. A sample was taken for analysis using the standard solution method (Greenberg et al 1992) and the spectra recorded. The probe remained in the water and a sample taken when an absorbance change was evident. There were a total of 5 samplings. The concentration measurements obtained using the probe were compared to a previously validated methodology (Lamontagne et al 1998).

To test the quantitative capabilities of the composite probe, a series of flasks containing 100 ml of seawater and two coupons (total area = 79.0 cm^2) were shaken. Each coupon was the same size and coated in the same manner. At one hour intervals, a flask was removed, part of the seawater taken for conventional spectrophotometric analysis using BCS (Greenberg et al 1992), and the remainder used for testing the composite probe. Solutions tested with the conventional analysis contained 103 ppb Cu(I), 280 ppb Cu(I), 395 ppb Cu(I), and 1020 ppb Cu(I) respectively. The composite probe was placed into the solution and the absorbance measured from 400 to 800nm at t=15 min. The resulting absorbance values at λ_{max} of 467nm were used to construct a calibration curve.

An "unknown" sample was prepared by shaking a sample of sea water with two anti-foulant coated coupons for 24 hours. The unknown was analyzed by the conventional spectrophotometric technique and with the fiber optic probe.

RESULTS AND DISCUSSION

The absorption spectra from the standard method of measuring varying standard concentrations of copper(I) using the BCS are in Figure 2A. The copper(I)-BCS complex exhibits a peak maximum at 484 nm. Figure 2B represents an absorption spectrum obtained from the composite probe measurement of copper(I) in solution. The probe has a peak maximum at 467 nm.

In the first experiment, the probe was placed in 2 L of stirred seawater with three anti-foulant paint coupons and was monitored continuously as described above. Figure 3 is a plot of copper(I) concentrations read by the probe over time. The concentration values plotted were obtained by analyzing an aliquot of seawater using the standard solution method. Resulting data indicates that the probe reaches a steady state after about 250 minutes. The data fit to a fourth order polynomial distribution (ppb (y) = -0.92620 + 3.7838X - 2.7221e-2X^2 + 1.0188e-4X^3 - 1.3843e-7X^4; where r= 0.997)[1].

Figure 4 is a plot of the absorbance obtained using the composite probe. The copper(I) concentrations were verified using the Standard Solution method. The data fit a second order polynomial (ABS = $2.97 \times 10^{-4} - 4.46 \times 10^{-5}X + 1.28 \times 10^{-6}X^2$; where r = 0.986)[2]. Line curvature at lower copper(I) concentrations is most likely a result of mass transfer effects (16).

The response of the composite probe to an "unknown" sample is shown in Figure 5 (solid diamond). The unknown falls almost on the calculated line from the linear regression analysis (ABS = $1.92 \times 10^{-3} + 1.11 \times 10^{-4}$ X where r= 0.977) [3]. Using this equation, the concentration of copper(I) in the unknown, calculates as a value of 118ppb copper(I). The actual concentration of copper(I) in the unknown was 101 ppb as determined by the conventional spectrophotometric analysis. Hence, the calculated concentration of copper(I) in the unknown is within 17% of the measured concentration of copper(I).

The spectrum of the calibration sample containing 101 ppb was used to calculate the detection limit for the system. By taking three times the standard deviation of the spectral noise in the system, a detection limit of 17 ppb was calculated for this probe.

While the probe is capable of detecting copper(I) in seawater at ppb levels, there also exists a need to detect copper(II) in the same water. The standard method for measuring total copper in seawater requires that all copper(II) be reduced to copper(I) using a reducing agent such as hydroxylamine hydrochloride(13). In the same way, it should be possible to measure copper(II) using the Nafion/C_{18}/BCP fiber optic composite probe.

In order to test this, a coupon was soaked in a 100 ml sample of seawater for 24 hours. After 24 hours, the seawater was partitioned into two aliquots; one to be analyzed using the standard spectrophotometric analysis, and the other by the composite probe. Analysis of the seawater sample using conventional spectrophotometric analysis indicated a copper(I) concentration of 100 ppb, and a total copper concentration of 1000 ppb.

The composite probe was immersed in the second aliquot and the response was monitored before and after the addition of hydroxylamine-hydrochloride. A plot of the probe response is shown in Figure 6. Initially, the absorbance increases slowly due to the low concentration of copper(I) present.

After addition of hydroxylamine hydrochloride to the sample, the absorbance increases rapidly. This change in absorbance is due to the reduction of the copper(II) in the sample to copper(I). The two data sets are fit using regression analyses resulting in the following equations:

- Copper(I): $ABS = 2.3x10^{-3}(t, min) + 2.8x10^{-2}$ where $r = 0.995$ [4]

- Total Copper: $ABS = 1.2x10^{-2}(t, min) - 5x10^{-1}$ where $r = 0.994$ [5]

The rate of formation of the copper(I)-BCP complex can be determined from the slope of the line. Formation is five times faster for the solution containing hydroxylamine hydrochloride than for the sample with no hydroxylamine hydrochloride. This demonstrates that the probe response time can be related to the concentration of copper(I) in the sample. Thus, the composite probe is useful to first measure copper(I) in seawater. Additionally, by reducing the copper(II) in solution to copper(I), the probe can monitor the total ionic copper concentration, thus validating a methodology for the determination of both copper(I) and copper(II) in seawater.

The fiber optic probe under investigation was constructed from a solution of the ionomer Nafion and C_{18} liquid phase solid support infused with the bathocuproine (BCP) reagent. Previous investigations indicated that ppb level sensitivity could be achieved using this approach (11). This preliminary research has also demonstrated the ability to measure ppb concentrations, with a detection limit of 17 ppb. Our initial work focused on the detection of copper(I) alone, which is facilitated by the high formation constants for copper(I) over copper(II) and all other metal ions with the bathocuproine ligand. However, it is also of interest to be able to measure total copper since both copper(I) and copper(II) are biocides. Therefore, by first measuring the sensor response to copper(I) and then reducing all the copper(II) to copper(I), this study has demonstrated that both oxidation states of copper can be measured using the probe.

CONCLUSIONS

Total available ionic Copper [(I) and (II)] is a potentially toxic trace metal controlled in the marine/estuarine environment by the chemistry of the water column (pH, salinity, ligands) and physical factors (currents, dilution, tides, suspended sediments). Thus anti-fouling paint containing Cu(I) presents a challenge to the environment because its design is to leach continuously over a period of time. The copper is a biocide that kills or prevents attachment of

organisms to a ship hull, but, also, becomes a source of introduced Cu(I) and eventually Cu(II) to the environment.

The conclusions from this phase of the study are:

- that the chemical procedure using the BCP C_{18} polymer bead is a way to test for total available ionic copper [(I) and (II)];
- that the chemical procedures are reproducible and robust; and
- that the C_{18} polymer bead presents a method for further study.

Further field testing is necessary.

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Figure Legends

Figure 1. Schematic of the experimental set-up (Anon. 1998).

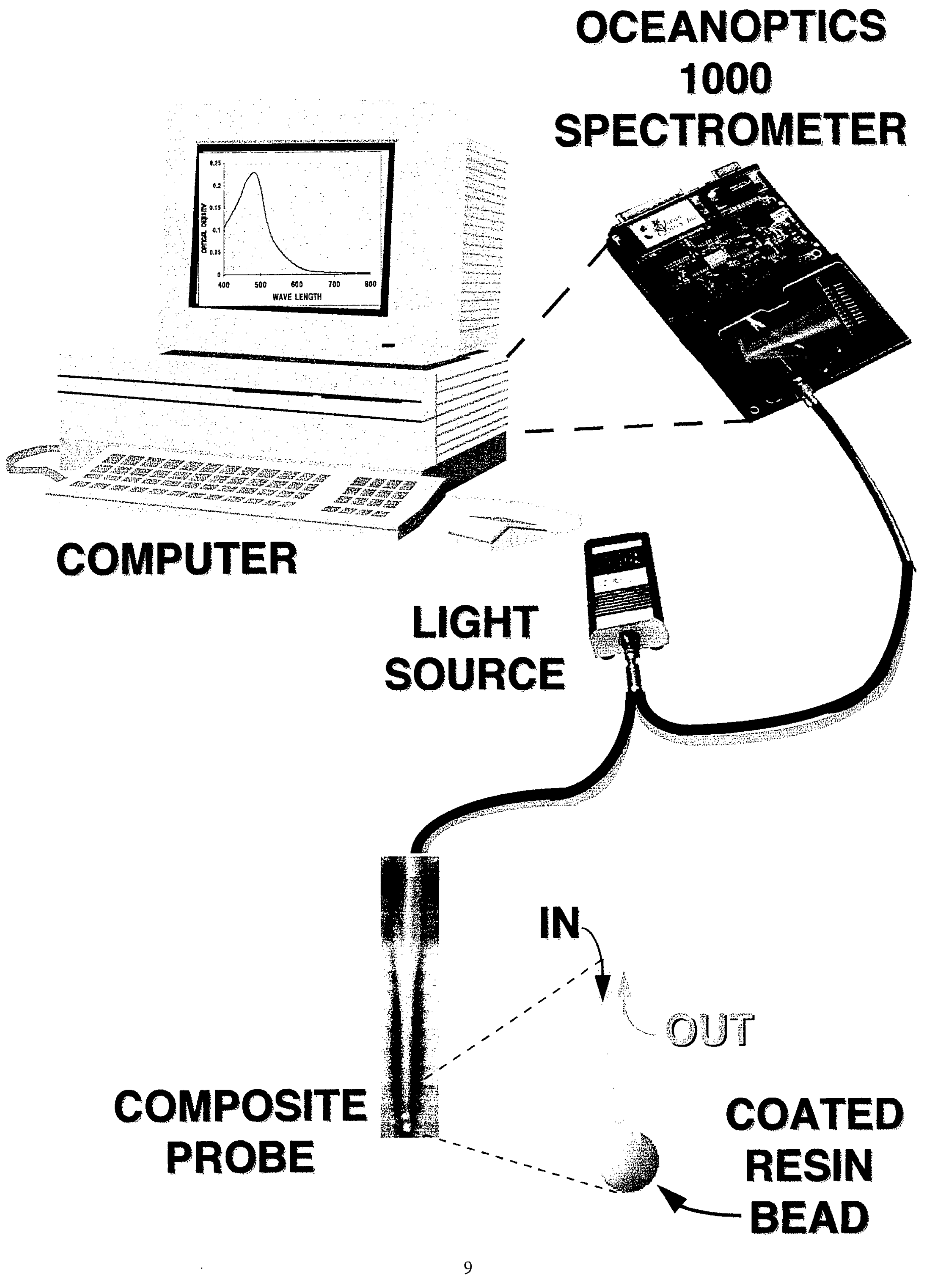
Figure 2. Comparison of absorption spectra from: A) the standard BCS method for copper; B) the experimental fiber optic probe.

Figure 3. Response of the fiber optic composite probe to varying concentrations of copper(I).

Figure 4. Absorption versus copper(I) concentration from fiber optic probe.

Figure 5. Comparison of an unknown sample to known copper(I) concentration samples.

Figure 6. Response of the composite fiber optic probe to the addition of hydroxylamine hydrochloride.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SPECTROMETER
0.25
0.2
0.15
0.1
0.05
0
OPTICAL DENSITY
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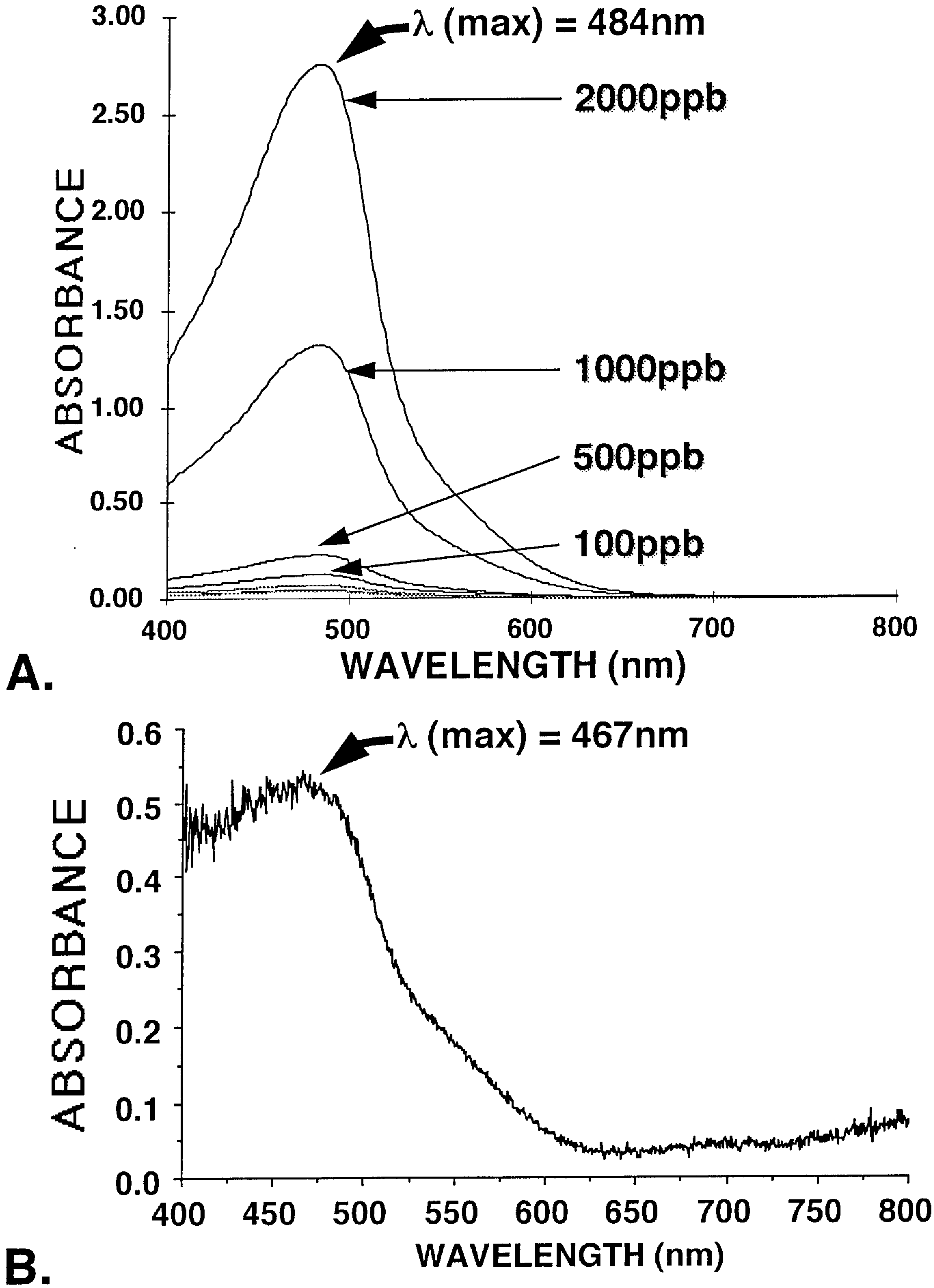
600
700
800
WAVE LENGTH
COMPUTER
LIGHT
SOURCE
IN
OUT
COMPOSITE
PROBE
COATED
RESIN
BEAD



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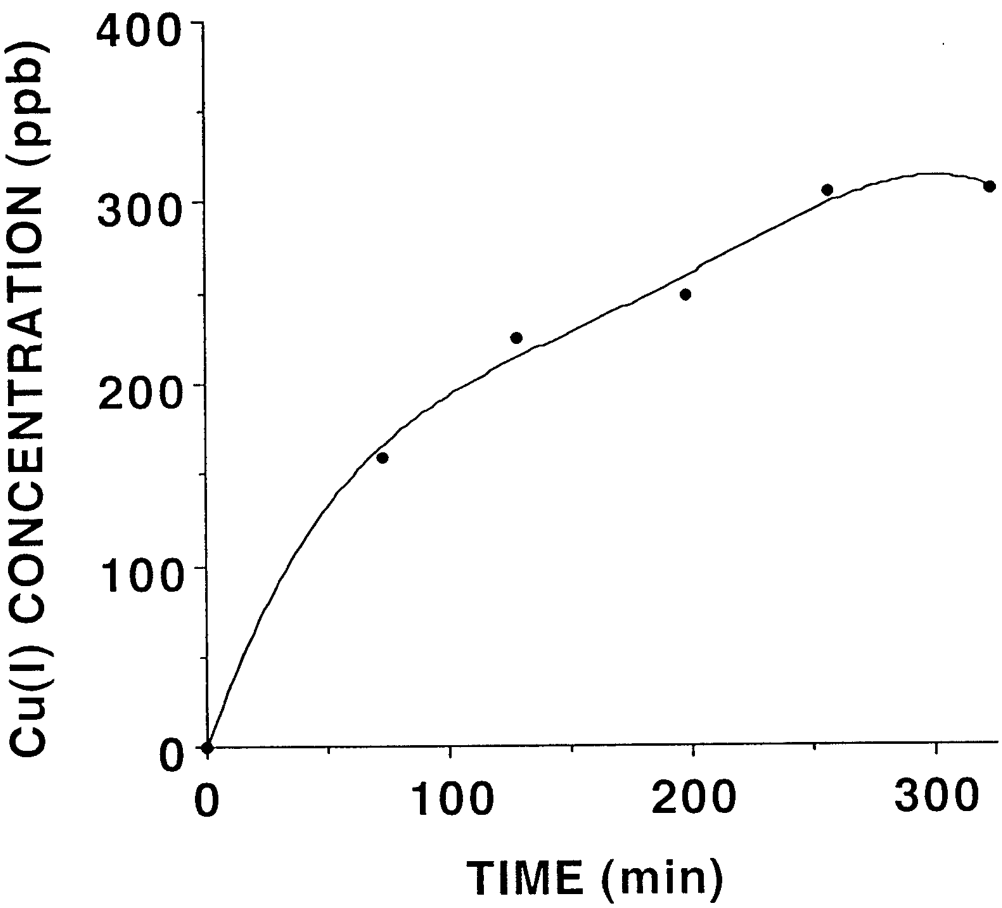
1000ppb
500ppb
100ppb
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ABSORBANCE
400
500
600
700
800
WAVELENGTH (nm)
A.
λ (max) = 467nm
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE
400
450
500
550
600
650
700
750
800
WAVELENGTH (nm)
B.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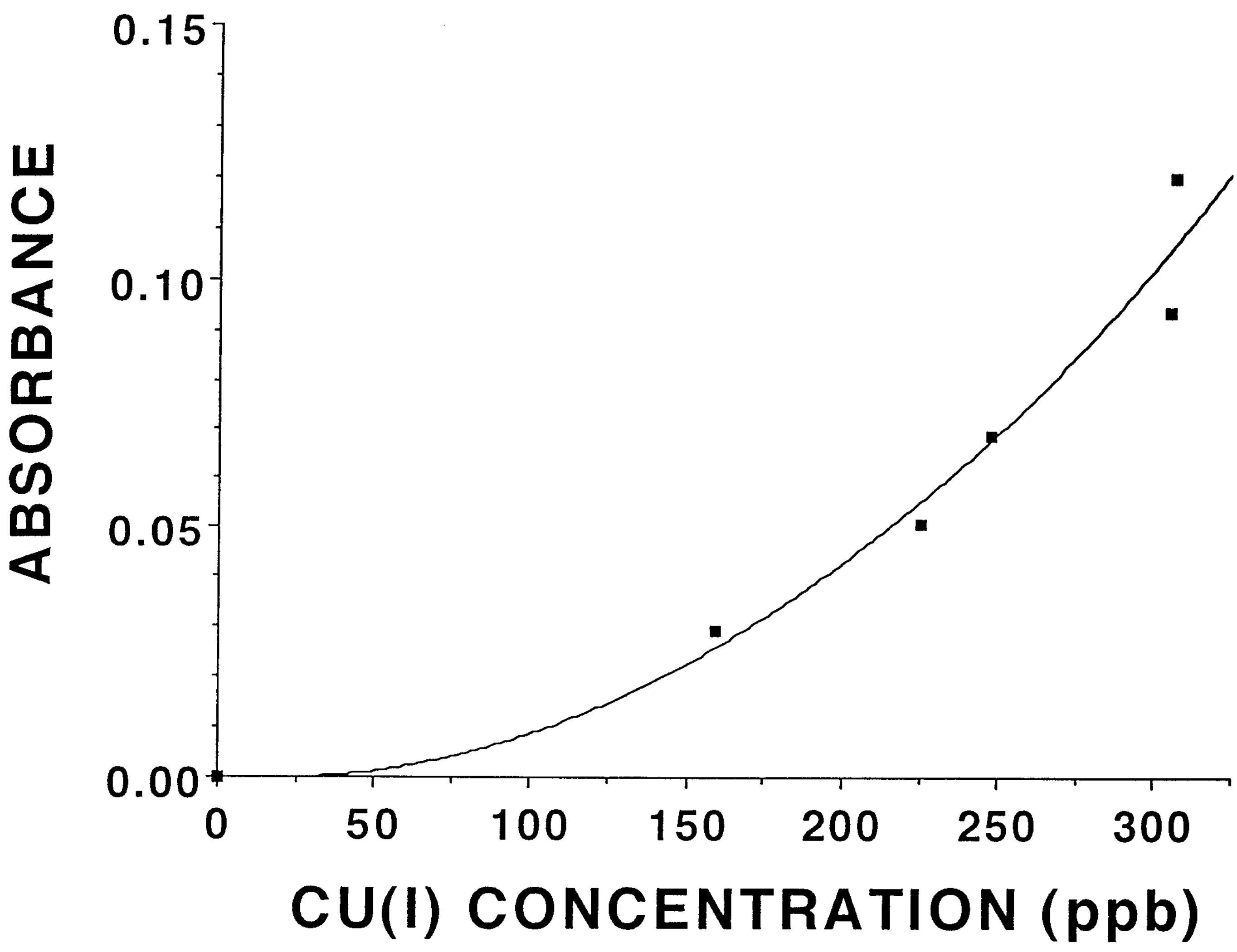
100
200
300
TIME (min)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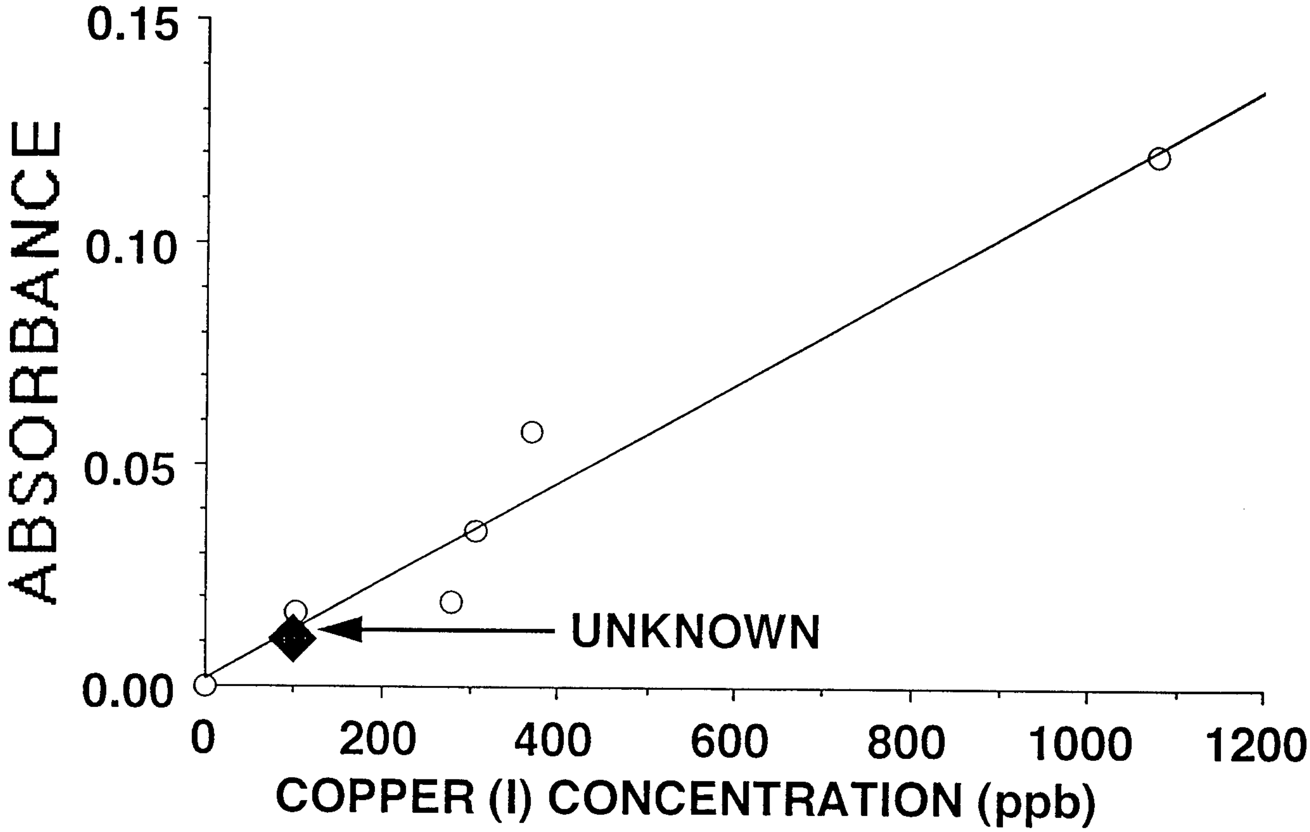
50
100
150
200
250
300
CU(I) CONCENTRATION (ppb)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0.10
0.05
0.00
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UNKNOWN
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800
1000
1200
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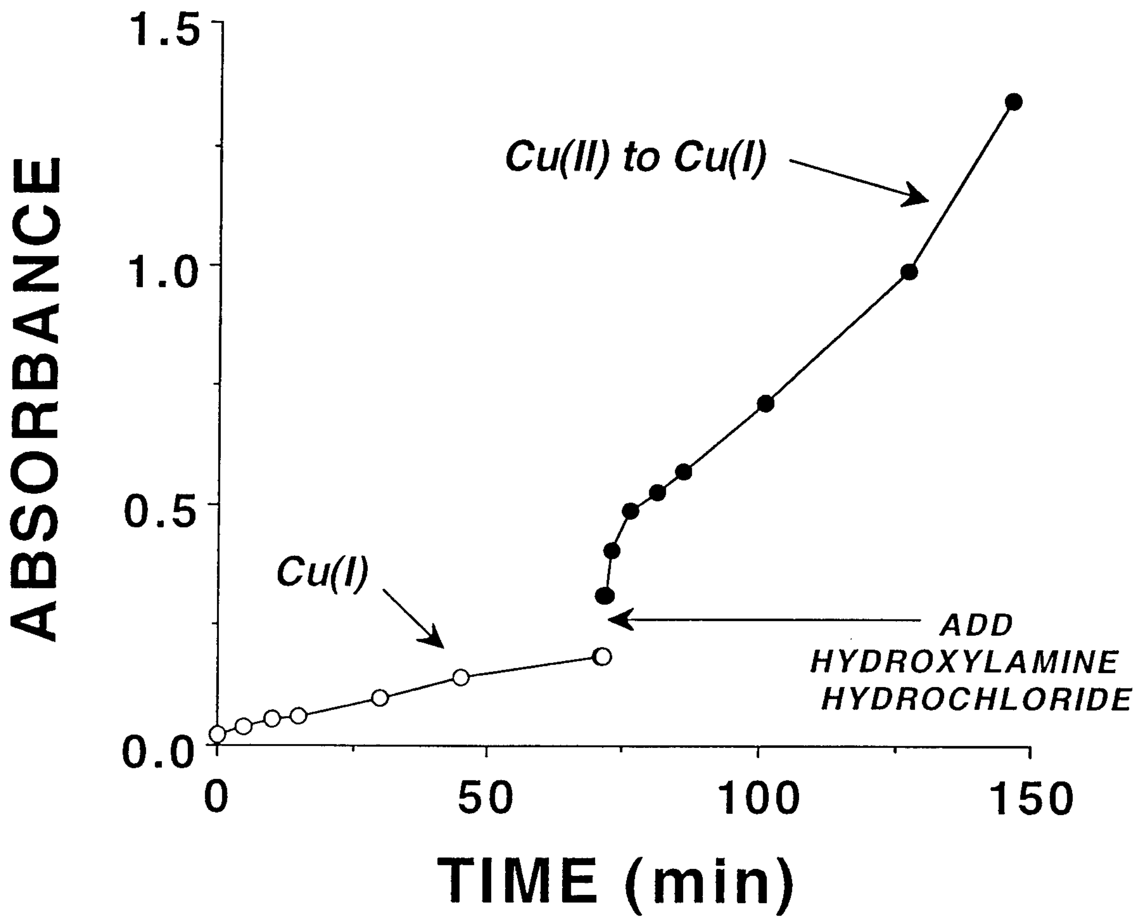
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1.0
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0.0
ABSORBANCE
Cu(II) to Cu(I)
Cu(I)
ADD
HYDROXYLAMINE
HYDROCHLORIDE
0
50
100
150
TIME (min)